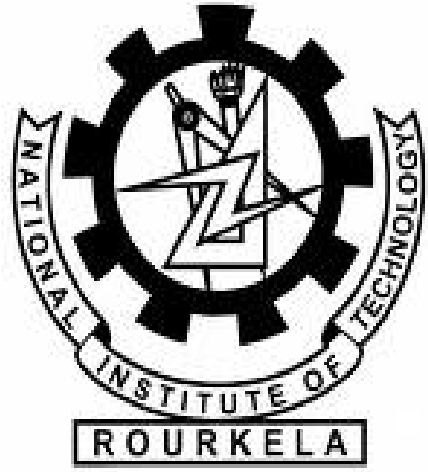
SYNTHESIS AND CHARACTERISATIONS OF $BaBi_4Ti_4O_{15}$ ceramic

A REPORT SUBMITTED TO

DEPARTMENT OF PHYSICS

NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA



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CERTIFICATE

This is to certify that the thesis entitled submitted by Miss. Bindushree Sahoo in partial fulfilments for the requirements for the award of Master of Science Degree in Physics Department at National Institute of Technology, Rourkela is an authentic work carried out by him under my supervision and guidance. To the best of my knowledge, the matter embodied in the project has not been submitted to any other University/ Institute for the award of any Degree or Diploma.

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DECLARATION OF THE CANDIDATE

I here by declare that the project work entitled **"SYNTHESIS AND CHARACTERISATION OF $BaBi_4Ti_4O_{15}$"** is an authentic work carried by me, during the one year project at NIT, Rourkela, from July 2011 to May 2012 under the supervision of PROF.S.PANIGRAHI and is being submitted for the partial fulfillment of the requirement for award of the degree of Master of Science in Physics to NIT, Rourkela. This has not been submitted anywhere else for the award of any other degree.

Date 14.5.2012 **Bindushree sahoo**

ACKNOWLEDGEMENT

Before presenting the thesis work, I would like to mention a few words for the people who gave their complete support for my thesis work.

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Date :15.05.2012 BINDUSHREE SAHOO

CONTENTS

ABSTRACT:

Bi-based Aurivillius family of compounds have received considerable attention as materials for ferroelectric random access memory (FRAM) because of their low operating voltage, field, superior polarization fatigue resistant characteristics and high Curie temperature . A large remnant polarization, low coercive field and high Curie temperature are required for better performance of FRAM devices. Barium-Bismuth titanate, $BaBi_4Ti_4O_{15}$ (BBT), a member of aurivillius bismuth based layer structure Perovskite was prepared from solid state method of low energy ball-milling process. The XRD analysis of calcined powders confirms the single phase formation. SEM was taken for sintered pellet of different duration to study the surface morphology. The microscopic image supposed Ba^{+2}addition leads to changes in the microstructural development, particularly in the change of the average grain size. Dielectric measurement is carried out to confirm its relaxor behaviour.

CHAPTER 1

INTRODUCTION

1.1 Dielectric Phenomena:

Dielectric materials are unlike semiconducting materials have large energy band gap so that thermally excited charge carriers are absent in these materials. mostly it behave as an insulator. But unlike insulator it has the ability to be polarized i.e charge ordering when subjected to mechanical stress, electric, magnetic or electromagnetic field and thermal variation. When a dielectric material responds above causes, it shows various effects like piezoelectricity, pyroelectricity, ferroelectricity etc. these different dielectric phenomena can be exploited to a large scale day to day application in capacitors, actuators, transducers, sensors, memory applications etc.

1.1.1 piezoelectricity: Some dielectric materials are seen of developing voltage across their surface when subjected to mechanical stress. This property is known as piezoelectricity. This is due to the formation of dipole moment as a result of the shifting of charge centres. This is known as Direct piezoelectric effect. The reverse effect can also be realized i.e when such type of material are subjected to electric field stress, then mechanical strain develops within, which is known as reverse piezo electric effect. Out of 32 point groups of crystal classes , 20 classes of non-Centro symmetric group show this phenomenon.

1.1.2 Pyroelectricity: Some non centrosymmetric crystal classes are characterized by unique polar axis i.e dipole moments of local regions contribute a non zero value along a particular axis. This gives a spontaneous polarization even in the absence of electric field. Ten out of the twenty non Centro symmetric classes are showing unique polar axis. When such type of matetrials are subjected to any thermal variation, voltage appears in their surface due to growth of spontaneous polarization. This phenomenon is termed as pyroelectricity.

1.1.3 Ferroelectricity: Spontaneous polarization exists in pyroelectric materials are seen of behaving differently in an oscillating field. Some materials are tested of non-switch ability of spontaneous polarization with changing of cycles where as some responds accordingly. The

property shown by some pyroelectric materials of reversing their orientation as per the electric field is known as ferroelectricity.

1.2 Basis of Ferroelectricity:

Ferroelectricity is a property shown by some materials possessing reversible spontaneous polarization. These materials are characterized by high dielectric constant, piezoelectric coefficient, pyroelectric coefficient as well as electromechanical coupling constant. one of the most fascinating properties of dielectric solids. Materials exhibiting ferroelectric properties must be either single crystals or polycrystalline solids composed of crystallites; they must also possess reversible spontaneous polarization. The term ferroelectricity was coined by only because of the structure analogy between the electrical behavior of such dielectrics and the magnetic behaviour of ferromagnetic compound.A ferroelectric may therefore consider to be an electric magnet. IN solid state physics, ferroelectricity is often interpreted as phenomena of network dynamics or as vibration of phonons.In solid state chemistry, the approaches are much closer to the realm of crystallography than to that of spectroscopy.

The polar properties of classical ferroelectrics become apparent only below temperature Tc termed the Curie temperature. The high temperature state is referred to as being paraelectric. A ferroelectric crystal is usually composed of domains, distinct areas is small n which polarization occurs uniformly in the same direction and orientation.When the polarization of the dielectric can be altered by an electric field, it is called ferroelectric. Ferroelectric materials are generally single crystal or polycrystalline ceramic oxides. Ferroelectric materials belong to pyroelectric family. Ceramics are the single crystals because they are easy to synthesize. The first known ferroelectric material found was Rochelle salt in 1921. Then Barium Titanate (BaTiO3) was discovered to ferroelectric material.

1.2.1 HYSTERSIS LOOP

Fig.1 is the diagram of P-E loop. We are getting that if we are increasing the field strength the domains start to align in the positive direction which gives rise the increase in polarization. After a certain field the polarization reaches a saturation value. Then if the external field is removed the polarisation does not fall to zero, some polarization is there and this is called remanant

polarization. The crystal cannot be completely depolarised until a field of magnitude (OF) is applied and this field is called coercive field (Ec).If the field is increased to more negative value direction of polarisation flips and hence a hysteresis loop is obtained

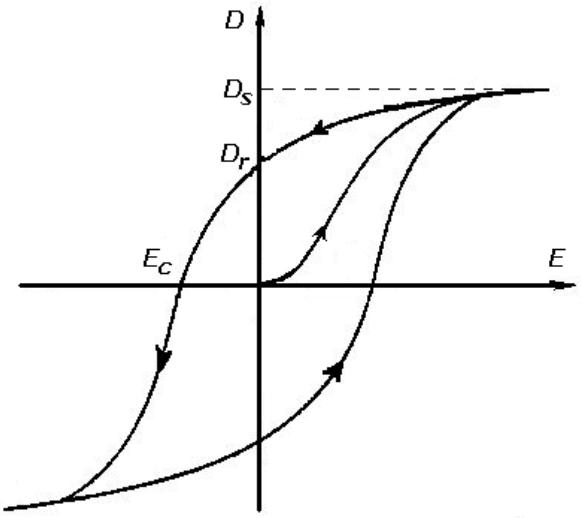


Fig.1

Ferroelectric structure

1. Pervoskite structure

2. Bismuth layered structure

3. Tungsten-Bronze structure

4. Pyrochlore structure

1.2.2 Ferroelectric domains:

Ferroelectric domains are nano regions inside the volume of the materials having different dipole moment orientation. In the absence of the external field, domains are aligned randomly cancelling each others effect. When the sample is under zero field and strain-free conditions, all the domain states have the same energy; but if an electric field is applied, the free energy of the system is lowered by aligning the polarization along the field. Thus, large applied electric fields can permanently reorient the polarization between the allowed domain states, which are restricted by crystallography. As a result, even ceramics, constituted by polycrystals randomly oriented can be electrically poled to produce net piezoelectric coefficients. Much of the importance of ferroelectric materials is due to their properties, leading to a wide range of applications. Among these applications are high dielectric constant capacitors, piezoelectric sonar, ultrasonic transducers, ultrasonic motors, actuators and pyroelectric detectors. Special mention is reserved for the ferroelectric memories, field effect and cooling devices.

1.2.3 Types of ferroelectric material

Ferroelectrics material can be classified as two types basing on its transition from ferroelectric to paraelectric behaviour, such as 1)-Normal ferroelectric 2)-Relaxor ferroelectric

Normal ferroelectric materials: These type of material are characterised by sharp phase transition at curie point depends feebly on frequency. They are following curie-Weiss law. Mostly they have high remnant polarisation, behave anisotropically with light.

Relaxor ferroelectric materials: These type of materials are characterised by broad diffused phase transition and are strongly responding the changes in frequency. They follow Curie-Weiss square law. Mostly possess low remnant polarisation and have weak anisotropic behaviour with light.

1.2.4 Diffuse Phase Transition

Many phase transitions in macroscopic homogeneous materials are characterized by the fact that the transition temperature is not sharply defined. In these, so-called diffuse phase transition temperature (DPT), the transition is smeared out over a certain temperature interval, resulting in a gradual change of physical properties in this temperature region. Though this phenomenon is

observed in several types of materials , however, the most remarkable examples of DPT are found in ferroelectric materials . Ferroelectrics diffuse phase transitions (FDPT) are first mentioned in the literature in the early 1950's. Some characteristics of the DPT are: (a) broadened maxima in the permittivity- temperature curve, (b) gradual decrease of spontaneous and remanent polarisations with rising temperature, (c) transition temperatures obtained by different techniques which do not coincide, (d) relaxation character of the dielectric properties in transition region and (e) no Curie-Weiss behavior in certain temperature intervals above the transition temperature. The diffuseness of the phase transition is assumed to be due to the occurrence of fluctuations in a relatively large temperature interval around the transition. Usually two kinds of fluctuations are considered: (a) compositional fluctuation and (b) polarization (structural) fluctuation. From the thermodynamic point of view, it is clear that the 18 compositional fluctuation is present in ferroelectric solids-solutions and polarization fluctuation is due to the small energy difference between high and low temperature phases around the transition. This small entropy difference between ferroelectric and paraelectric phase will cause a large probability of fluctuation. Kanzing has observed from X-ray diffraction that in a narrow temperature range around the transition $BaTiO_3$ single crystal splits up into FE and PE micro regions. According to Fritsberg substances of less stability are expected to have a more diffuse transition. For relaxor as well as other FDPT the width of the transition region is mainly important for practical application.

1.2.5 Ferroelectric Application:

The nonlinear nature of ferroelectric materials can be used to make capacitors with tunable capacitance. Typically, a ferroelectric capacitor simply consists of a pair of electrodes sandwiching a layer of ferroelectric material. The permittivity of ferroelectrics is not only tunable but commonly also very high in absolute value, especially when close to the phase transition temperature. Because of this, ferroelectric capacitors are small in physical size compared to dielectric (non-tunable) capacitors of similar capacitance.

The spontaneous polarization of ferroelectric materials implies a hysteresis effect which can be used as a memory function, and ferroelectric capacitors are indeed used to make ferroelectric

RAM for computers and RFID cards. In the applications thin films of ferroelectric materials are typically used, as this allows the field required to switch the polarization to be achieved with a moderate voltage. However, when using thin films a great deal of attention needs to be paid to the interfaces, electrodes and sample quality for devices to work reliably.

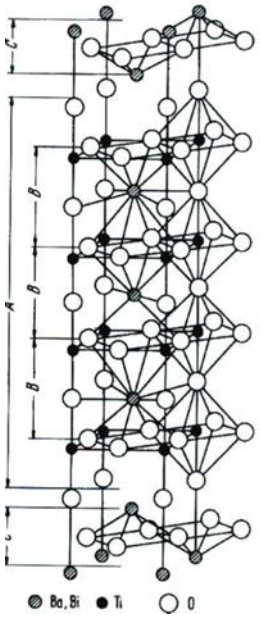
Ferroelectric materials are required by symmetry considerations to be also piezoelectric and pyroelectric. The combined properties of memory, piezoelectricity, and pyroelectricity make ferroelectric capacitors very useful, e.g. for sensor applications. Ferroelectric capacitors are used in medical ultrasound machines (the capacitors generate and then listen for the ultrasound ping used to image the internal organs of a body), high quality infrared cameras (the infrared image is projected onto a two dimensional array of ferroelectric capacitors capable of detecting temperature differences as small as millionths of a degree Celsius), fire sensors, sonar, vibration sensors, and even fuel injectors on diesel engines.

Another idea of recent interest is the ferroelectric tunnel junction (*FTJ*) in which a contact made up by nanometre-thick ferroelectric film placed between metal electrodes. The thickness of the ferroelectric layer is small enough to allow tunneling of electrons. The piezoelectric and interface effects as well as the depolarization field may lead to a giant electro resistance (GER) switching effect.

1.3 THESIS OBJECTIVE

Bi-based Aurivillius family of compounds is generalized as Bi2An-1BnO3n+3. The crystal structure consist of `n` number of (An-1BnO3n+3)2- slabs sandwiched between (Bi2O2)2+ layers, where `A` represents monovalent, divalent or trivalent elements and `B` represents trivalent, pentavalent or hexavalent metallic cations which are in 12-fold and 6-fold coordination, respectively. Our present work deals with the compound BBT with `n`=4 and structural formula as (Bi2O2)2+(BaBi2)Ti4O13)2-, where the Ba- and Bi-ions occupies the A-site and Ti-ions resides in the B-site, respectively.Synthesis of BBT ceramics is mainly based on chemical and solid-state reaction methods. BBT can be also produced by conventional solid-state reaction starting from BaCO3, TiO2, Bi2O3. The solid-state reactions initiated by intensive milling in high-energy ball mills could be a good choice for ceramic powder preparation.

- To synthesize ($BaBi_4Ti_4O_{15}$) by solid state route method.
- To go for the study of XRD for phase formation, SEM for surface morphology and electrical study for dielectric constant and transition temperature of the synthesized Material
- To study the relaxor behaviour of the material.



Chapter-2

Literature review

Bismuth layer structured ferroelectrics (abbreviated as BLSFs)have attracted considerable interest for their potential applications in non-volatile random access memory (NVRAM) and high temperature piezoelectric devices . The general chemical formula for BLSFs is $(Bi_2O_3)^{2+}$ $(A_{m-1}\ B_m\ O_{3m+1}\ )2-$, where A is mono-, di or trivalent cations (e.g., Ba^{2+} , Ca^{2+} , Pb^{2+} , Bi^{3+} , Na^{+} , or K^{+}), B is tetra,penta or hexavalent cations of a transition metal (e.g., Ti^{4+} , Nb^{5+} ,Ta^{5+} , or W^{6+}), and m is the number of perovskite-like layers (m = 1,2, 3, 4, 5) . The crystal structure of these compounds is composed of $(Bi_2O_2\ )^{2+}$ layers interleaved with perovskite-like blocks(Am−1 Bm O3m+1 $)^{2-}$. This reflects the fact that there exists a good possibility for mutual dopings within these various elements or with some other ions to BLSFs. Generally, the doping could be in bismuthoxide layer and/or in perovskite-like units (A or B sites).$BaBi_4Ti_4O_{15}$ (abbreviated as BBT), as the m = 4 member of the Aurivillius family has Ba and Bi ions at the A sites and Ti ion at the B sites of the perovskite $(A_{n-1}BnO_{3n+3}\ )^{2-}$ block $((Bi_2O_2\ )^{2+}((BaBi_2\ )Ti_4O_{13}\ )^{2-}$). Since its discovery by Aurivillius in 1949 ,BBT has attracted considerable attention duo to its high Curie temperature of about 417 °C and excellent ferroelectric properties. Pribosic et al. reported that the dielectric constant and Curietemperature of the BBT compound were increased insignificantly influence of lanthanum doping on the dielectric, ferroelectric and relaxor behavior of barium bismuth titanate ceramics and found that La^{3+} doping did not affect the crystal structure of BBT. At the same time, the diffuseness increased with increasing lanthanum content and partial doping could enhance the ferroelectric proper-ties of BBT ceramic. Rout et al. reported the phase transition in $ABi_4Ti_4O_{15}$ (A = Ca, Sr, Ba) Aurivillius oxide prepared through a soft chemical route and found that the BBT ceramic showed a relaxor-like behavior near phase transition and the dielectric relaxation rate follows the Vogel–Fulcher relation with activation energy 0.02 eV and freezing temperature 362°C. However, there have been few reports of the influence of lanthanum substituting bismuth in A site on the microstructure and dielectric relaxor behavior of BBT ferroelectric ceramics. In this work, we have investigated the dielectric relaxor behavior of $BaBi_{4-x}La_xTi_4O_{15}$ (BBLT ,x= 0.0, 0.25, 0.50 and 0.75, abbreviated as BBT,

$BBLT_{25}$,$BBLT_{50}$ and $BBLT_{75}$, respectively) ceramics. An obvious relaxation transition from relaxor-like ferroelectrics to relaxor ferroelectrics,then to relaxor-like ferroelectrics was observed with the increase of lanthanum content.

At the beginning of 1960s Smolenskii et al.1 reported a considerable diffuseness of the phase transformation in Ba-based ferroelectrics with Bi-layered structure, $BaBi_2Ta_2O_9$ (BBT) and $BaBi_2Nb_2O_9$ (BBN). They also found that in solid solutions of $Ba_{1-x}Sr_xBi_2Nb_2O_9$ (BSBN) the degree of diffuseness gradually decreases with the substitution Ba^{2+} by Sr^{2+} thus leading to a sharp phase transition in $SrBi_2Nb_2O_9$ (SBN). Ferroelectrics, first discovered by Aurivillius, the oxygen octahedra blocks responsible for ferroelectric behaviour are interleaved with $(Bi_2O_2)^{2+}$ layers resulting in a highly anisotropic crystallographic structure where c-parameter[normal to $(Bi_2O_2)^{2+}$ layers] is much greater than a and b parameters of the orthorhombic cell. Later, it was observed that, along with the large crystallographic anisotropy, Bi-layered perovskites demonstrate highly anisotropic electrical properties, In ferroelectric switching occurs predominantly in the (a,b) plane leading to a low switchable polarisation and poor piezoelectric properties of ceramic samples. It was originally suggest that Bi_2O_2 layers leading to inhomogeneous distribution of Ba and local charge imbalance in layered structure. This was recently confirmed by X-ray and neutron diffraction experiment. Ba-induced disorder is a probable source of the diffuseness of the phase transformation and apparent relaxor behaviour in these materials .Recently, the interest in Bi-layered perovskites (especially in a thin layer form) was raised due to their excellent stability against repetitive switching (fatigue endurance).and useful piezoelectric properties. Sr-based layered perovskites, $SrBi_2Ta_2O_9$ (SBT) and SrBi2Nb2O9 (SBN), are currently the major candidates for new generation of non-volatile ferroelectric memories.In this regard, their Ba-based counter parts, BBN and BBT, are of great interesting view of tailoring the mechanism of polarisation switching and controlling the degree of diffuseness of the phase transitions in these technologically important materials. Another motivation of project work was to study the mechanism of the relaxor behaviour in highly anisotropic(layered) structure and compare it with the relaxation mechanism in conventional relaxors such as Pb(Mg,Nb)O3 (PMN) or Pb(La,Zr,Ti)O3 (PLZT) with almost isotropic crystallographic structure.

. Recently, these bismuth layered structured materials with m=4 have been intensively investigated as lead-free ferroelectric and piezoelectric materials. A number of pure and modified BLSFs have been investigated with a view to their dielectric and ferroelectric properties, especially high temperature piezoelectric characteristics . The effect of A-site substitution is more obvious than that of B-site substitution, since the cations at B sites are similar in size and do not play a major chemical bonding and the Curie temperature (Tc) could be established in ferroelectric Aurivillius oxides.

To improved the piezoelectric activity, the introduction of A site vacancies allowing ease of polarization was proposed. $Na_{0.5}Bi_{4.5}Ti_4O_{15}$ (NBT) and $BaBi_4Ti_4O_{15}$ (BBT) are members of this family with m=4. The four-layer Aurivillius phase piezoelectric ceramic NBT system is due to their high Curie temperature and outstanding piezoelectric and electromechanical properties at this composition . At room temperature NBT is orthorhombic with a=0.5427 nm, b/a =1.006 and c =4.065 nm, and undergoes a ferro-to paraelectric (orthorhombic A21am to tetragonal I4/mmm) phase transition at Tc = 655 ^{0}C . NBT is a classical ferroelectric with a sharp maximum of dielectric permittivity. Jannet et.al reported that the ferroelectric–paraelectric phase transition gradually changes from a normal, second order type to a relaxor-like behavior above 60 mol% barium $Na_{0.5}Bi_{4.5}Ti_4O_{15}$–$BaBi_4Ti_4O_{15}$ solid solutions. The Tc temperature decreases from 655^{o}C (NBT)to about 420^{o}C (BBT) with an increase in BBT concentration .

BaBi4Ti4O15 (BBT) powder was synthesized by a cost-effective soft chemical route. The precursor powder, a mixture of Bi-, Ba-oxalates and TiO_2 was calcined at 1000^{0}C to produce a pure phase.

BBT. Better homogeneity of the precursor and exothermic decomposition of oxalates had facilitated the formation of BBT phase at 600^{0}C onwards. The microstructure of sintered specimen showed the formation of randomly oriented plate like grains in the ceramics. The temperature dependence of dielectric constant at various frequencies explained the relaxor behavior of thesample. The value of critical exponent (=1.88) obtained from the modified Curie–Weiss law, confirmed the same. All these observations clearly suggest that BBT is a relaxor ferro-electric. Aurivillius phase compounds, $ABi_4Ti_4O_{15}$ A = Ca, Sr,and Ba , were synthesized by a modified chemical route,precipitating respective nitrate onto the surface of TiO_2 particles. XRD study showed that all compounds have orthorhombic symmetry at room

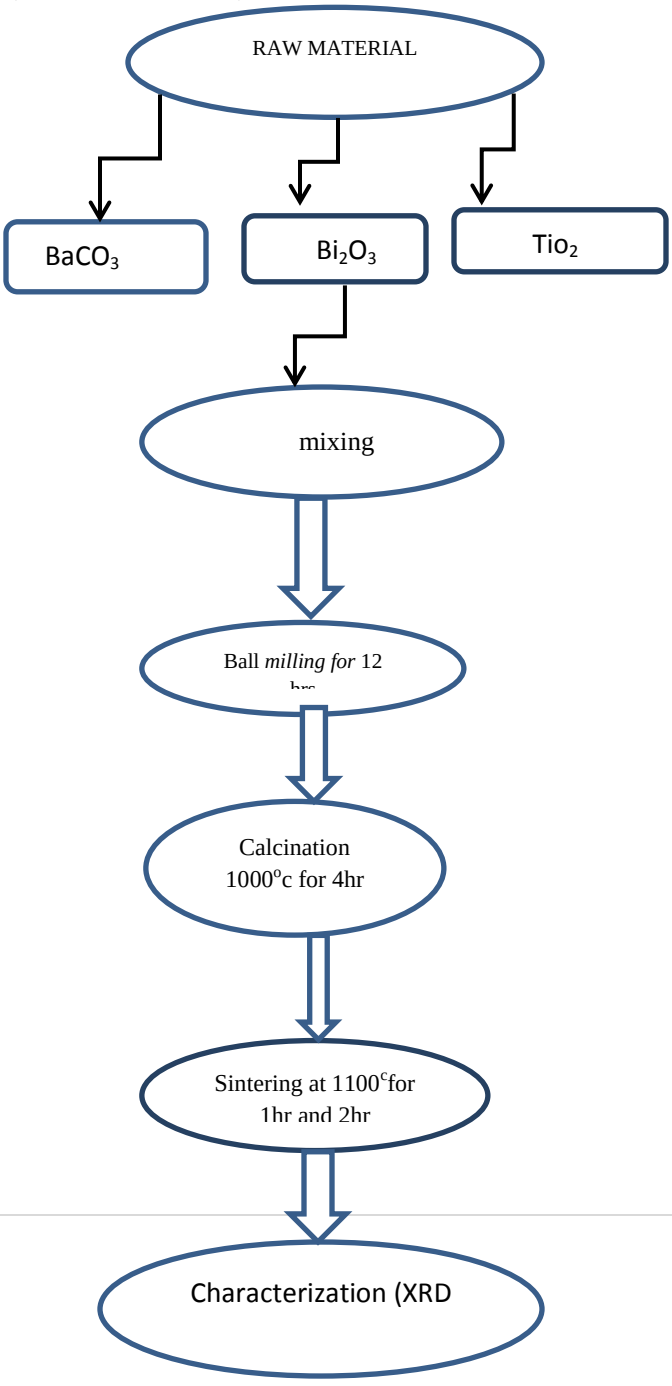
temperature. SEM micrographs confirmed the plate like grain. Temperature dependent dielectric study revealed that the CBT and SBT ceramics exhibit sharp transition normal ferroelectric behavior at 787^0C and525°C, respectively, whereas BBT showed a broad phase transition relaxor like ferroelectric behavior . Regarding the normal phase transition in CBT and SBT, in agreement with tolerance factor, a significant deformation of the perovskite block was observed.. The presence of a significant amount of foreign cations into the Bi_2O_2 slabs such as Ba^{2+} for$BaBi_4Ti_4O_{15}$, the incompatibility between the Ba^{2+} anionic environment, and the configuration of the Bi_2O_2 slabs become more subtle, and at a local scale the continuity of the Bi_2O_2 slabs cannot be ensured. Existences of such faults or mismatch in the layers stacking within the crystal may be the major cause for the observed relaxor behavior in BBT ceramic.

CHAPTER-3

3.1 EXPERIMENTAL TECHNIQUES

A basic introduction about the experiment use in synthesized and characterized the $BaBi_4Ti_4O_{15}$ ceramic compound. Synthesis of BBT ceramics is mainly based on chemical and solid-state reaction methods. BBT can be also produced by conventional solid-state reaction starting from BaCO3, TiO2, Bi2O3. The solid-state reactions initiated by intensive milling in high-energy ball mills could be a good choice for ceramic powder preparation.

3.1.1 Synthesis of ($BaBi_4Ti_4O_{15}$)



3.1.2 Calcination

Calcination is a process of heating, without fusion, to change the physical or chemical constitution of substances. The objectives of calcination is , to remove water which is absorbed as water of crystallization or water of constitution, to remove CO_2, SO_2 and other volatile substances, to oxidise the substance completely or partially. Calcination is also done in the processes of firing, roasting and burning. Calcination is also referred as calcining. Chemically calcination can be defined as thermal decomposition process applied to substances and ores to bring about phase transition, removal of volatile fractions and thermal decomposition. Calcining process is done on the temperature below the boiling point of the substance subjected to calcination.

3.1.3 Sintering

When thermal energy is appled to powder compact, the compact is densified and the average grain size is increased, this process is called sintering and the basic phenomena occurring form this process is densification and grain growth. This process is used to produce density controlled materials or compound from metal or ceramic powder by applying thermal energy. Microstructural control means control of grain size, sintered density, and size and distribution of other phases including pores. In most of the cases microstructural control prepare a full dense body with fine grain structure.

3.2 Characterization methods:

The structure provides a variety of concepts, which describes on various scales; its mechanical, chemical or electrical may depends strongly on its internal structure. An understanding of the structure of the material has become essential in the worked of novel materials. A wide range of experimental methods are available for the evaluation of structure of material with high accuracy and precision. The structure and morphology studies are performed by using various techniques such as

1. X-ray diffraction analysis (XRD)
2. Scanning electron microscopy (SEM).
3. Dielectric study by LCR measurement
4. P-E loop tracer

3.2.1 X-Ray diffraction study:

X-ray powder diffraction (XRD) is a technique primarily used for phase identification of a crystalline material after the completion of synthesis process. A lot of information such as lattice structure, arrangement of atoms i.e atomic sites in a unit cell can be obtained by systematic analysis of XRD peaks. Unknown crystalline materials such as .minerals, inorganic compounds can be detected by studying X-ray powder diffraction patterns.

Other applications include

- To characterize crystalline materials
- To identify fine-grained minerals such as clays and mixed layer clays which are difficult to be determined optically.
- To determine unit cell dimensions
- To measure sample purity

It is often possible to separate the effects of size and strain. Where size broadening is independent of q (K=1/d), strain broadening increases with increasing q-values. In most cases there will be both size and strain broadening. It is possible to separate these by combining the two equations in what is known as the Hall-Williamson method:

$B.\cos\theta = (k\lambda/L) + \eta.\sin\theta$

Thus, when we plot B.cos (θ) vs. sin (θ) we get a straight line with slope η and intercept kλ/L.The expression is a combination of the Scherrer Equation for size broadening and the Stokes and Wilson expression for strain broadening. The value of η is the lattice strain and the value of L represents the size of the crystalline. The value of constant k is taken as 0.9.

When the highly energetic X-Ray beams strikes the atom of the crystal surface they scatter in different direction. In few directions these waves obey Bragg's condition.

$$i.e\ 2d\ \sin\theta = n\lambda$$

By XRD study we can know how the atoms are packed in crystals, interatomic distance, angle, phase composition.

3.2.2 Scanning Electron Microscope (SEM) Study:

A scanning electron microscope (SEM) is a technique of getting microscopic image of the surface exploiting the wave character of electron beams. it with a high-energy beam of electrons in a raster scan pattern. The electrons impinge on the surface of the sample and interact with the atoms that make up it produce signals which contain information about the sample's surface topography, composition, and other properties such as electrical conductivity. The sample size must be an appropriate to fit in the specimen chamber and are generally mounted rigidly on a specimen holder called a specimen stub. Several models of SEM can examine any part of a 6-inch (15 cm) semiconductor wafer, and some can tilt an object of that size to 45°. Back scattered electron imaging, quantitative X-ray analysis, and X-ray mapping of geological specimens and metals requires that the surfaces be ground and polished. The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens.

3.2.3 Dielectric Study by LCR meter:

Impedance measurement can be done with the help of a LCR meter for a varied number of applications. An LCR meter is not only used exclusively for component testing of inductors, resistors and capacitors but also employed in the electrical characterization of gases, chemicals, powders and other dielectric materials.

Dielectric, insulating material or a very poor conductor of electric current. When dielectrics are placed in an electric field, practically no current flows in them because, unlike metals, they have no loosely bound, or free, electrons that may drift through the material. Instead, electric polarization occurs. The positive charges within the dielectric are displaced minutely in the direction of the electric field, and the negative charges are displaced minutely in the direction opposite to the electric field. This slight separation of charge, or polarization, reduces the electric field within the dielectric. The presence of dielectric material affects other electrical phenomena.

The force between two electric charges in a dielectric medium is less than it would be in a vacuum, while the quantity of energy stored in an electric field per unit volume of a dielectric medium is greater. The capacitance of a capacitor filled with a dielectric is greater than it would be in a vacuum. The effects of the dielectric on electrical phenomena are described on a large, or macroscopic scale by employing such concepts as dielectric constant, permittivity and polarization.

3.2.4 P-E LOOP TRACER:

PE Loop tracer is designed for characterisation of materials such as ferroelectrics. The system measures the hysteresis loops for these materials. The broad specifications and main features are listed here below:

•High voltage power supply with overload protection, Digital potentiometer.

•Input 220V Ac, Output 5KV Max Current 20mA, Programmable AC source variable frequency

•Programmable AC source fixed frequency 20Hz to 1kHz,.Current limiting circuit.

•ISA/USB Data acquisition hardware to collect samples from the unit.

•Temperature hardware for measuring the temperature of sample bath, Signal conditioning hardware with unity gain amplifier.

•Signal conditioning hardware with unity gain amplifier, Analogue to digital converter hardware.

•Integrator selector (for selection of internal reference capacitor and resistance)

•Sample holder Heater 400 Dec C Ramp controller, Temperature measurement hardware.

•Minimum Sample Resistance 200 K Ohm, Software for measurement data recording and plotting.

•Consumables : Silicon Oil 100ml

PRINCIPLE OF MEASUREMENT

The presented measurement technique is based on the Sawyer-Tower method which was introduced to obtain hysteresis loops at ferroelectric samples. The sample is placed in series with a reference capacitor. This circuit is connected to a voltage source which generates here a step voltage Uo instead of a triangular signal (Figure a). The voltage at the capacitor Uc(t) can

be measured with an electrometer with high input impedance to avoid the discharge of the capacitor. From the voltage Uc(t) the charge Qc(t) on the capacitor can be calculated. The same charge is also present on the sample. With the area A of the sample the polarization P(t) can be derived from the charge, i.e. P(t) = Qc(t)IA. Hereby the reference capacitor should have at least a

capacitance 100 times larger than the capacitance of the sample. Then the voltage drop at the capacitor is negligible and the source voltage is nearly the same as the voltage at the sample.

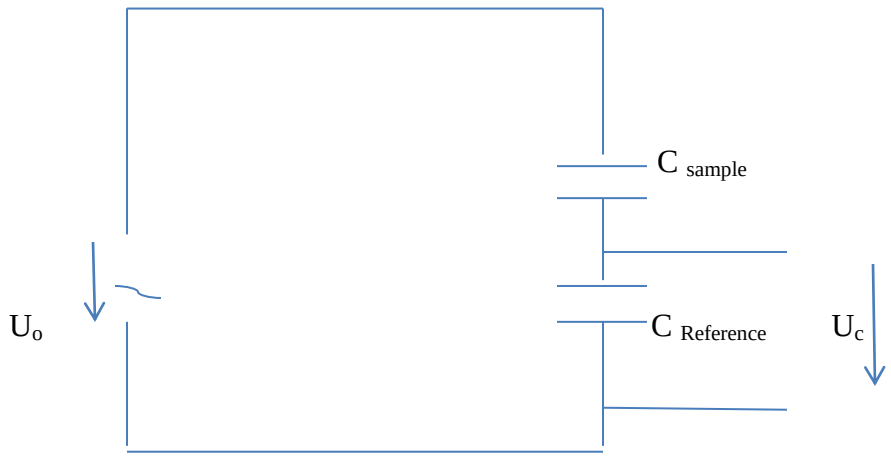


Fig-a

CHAPTER-4

4.1 Experimental work:

The $BaBi_4Ti_40_{15}$ ceramic were prepare by solid state reaction method by taking three raw materials such as, (i) Barium carbonate (ii) Bismuth oxide (iii) Titanium oxide.

- All the precursors having 99% purity, for the preparation of 23gms.The precursors are calculated in a stoichiometric ratio.
- The precursors are mixed thoroughly in dry condition in an agate motor for 2hrs .
- For proper mixing of mixture and ball milling technique. The process continued for 12hrs in the liquid medium using acetone. Then the mixture is dried and again the powders were grinded in an agate motor for 15 min.
- The dried powders are kept in crucible for calcination is the process for removal of volatile fraction. The calcination is carried out 1000oc for 4hrs and then cooled in the furnace.
- Again the calcined powders are grinded in an agate motor to get fine powder. Then I made pellet and sintered at 1100oc for 1hr and 2hr.
- For making pellet used binder(PVA)solution mix with powder and to make pellets by using hydraulic pressure to applying around 5ton pressure for 3min
- To know the phase formation of prepare sintered pellet used XRD technique. Use SEM for surface morphology and electrical property like P-E loop and dielectric measurement.

4.2 RESULT AND DISCUSSION:

4.2.1 XRD ANALYSIS:

Fig. 2 shows the XRD pattern of $BaBi_4Ti_4O_{15}$ ceramics calcined at 1000^oC for 4hr and sintered at 1100^0C for 2hr. Both of the XRD pattern tetragonal with space group *I4/mmm (139)* (JCPDS Card No: 73-2184) and initial cell parameters of changed from powder (a=b=3.86Å, c=41.76Å) to pellet (a=b=3.8624Å, c=41.851Å), which indicates the lattice parameters slightly increased due to compactness developed in the material sintering at 1100^0C .

	a	b	c	volume
BBT powder	3.825	3.825	41.9410	613.6230
BBT pellet	3.8624	3.8624	41.8510	624.3388

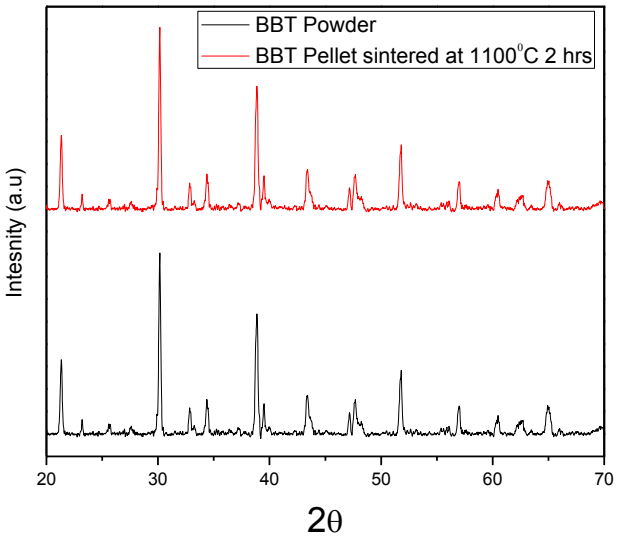


Fig-2

4.2.2 SEM (SCANNING ELECTRON MICROSCOPE) study:

The grain growth seems not completed for the pellet sintered at 1100^0C for 1 hr in fig 3. Still their exist some porosity which confirms densification is not completed. When sintering duration was increased to 2hr, grain growth appeared to complete in fig 4. Size of grain is non uniform, irregular but porosity is mostly absent.

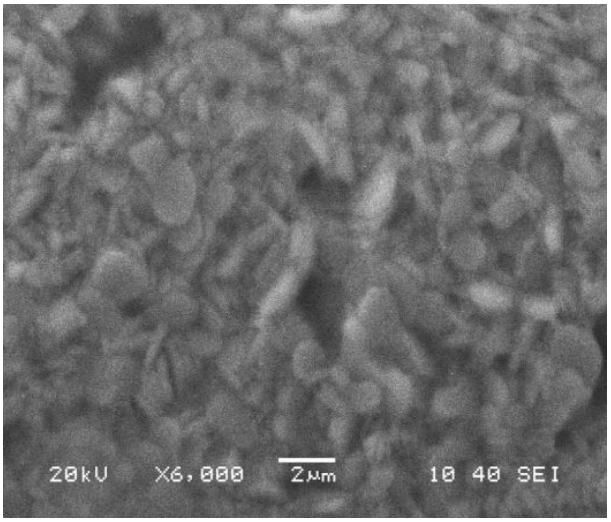


Fig-3

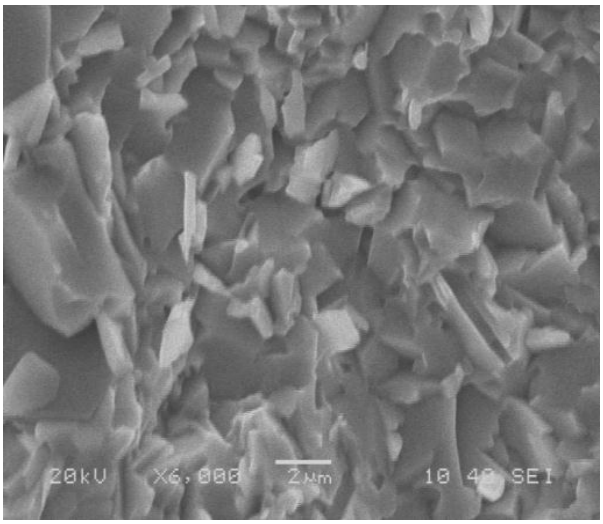


fig-4

4.2.3DIELECTRIC STUDY:

4.2.3.1-Relative permitivity study:

Dielectric measurement was taken by the help of an impedace analyser. Sintered pellet of 2hr duration was set for study. At low temperature , the dielectric constants for different frequencies are almost equal. With the rise in temperature the dielectric contant increases due to the activation of dipolar and space charge polarisation which are mostly temperature dependent. With increasing frequency the dielectric constant decreases as the relaxation time of dipolar and space charge polarisation are higher than the time period of cycle of oscillating field. The peak shows broadness having diffusivity character.T_c shifts towards the higher temperature with the increase in temperature. This confirms the relaxor property of the material. The dielectric loss increases with increase in temperature. This is due to mostly the development of leakage curent.

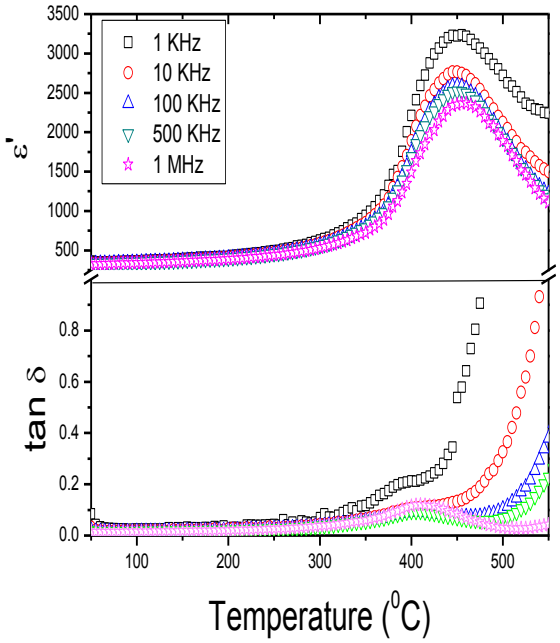


Fig-5

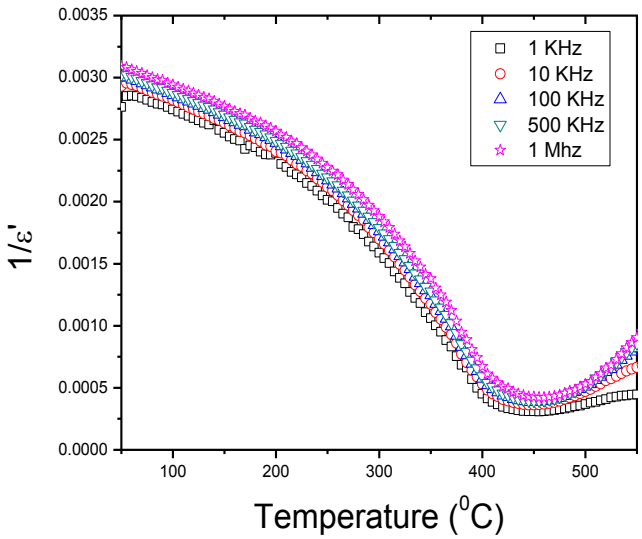


fig-6

4.2.3.2 IMPEDENCE STUDY:

Fig.8 shows the value of Z' decreases with increases in frequency as well as with temperature. This indicates an increase in ac conductivity of the system with increase in frequency and temperature. The reason for such behavior is due to the release of space charge due to reduction in the potential barrier of the material with rise in temperature. This is responsible for increase in ac conductivity of the material. At low frequency values of Z' decreases with rise in temperature suggesting the negative temperature coefficient type of behaviour .

Fig.7 shows Z" peak shifted to higher frequency with increasing frequency with increasing temperature implying existence of distribution of relaxation time with temperature .Thus it can be said that present system possesses temperature dependent relaxation process peak indicates non-debye type behaviour. The peaks in asymmetric in nature suggesting the material to be consisting of electrical processes with spread of relaxation time.

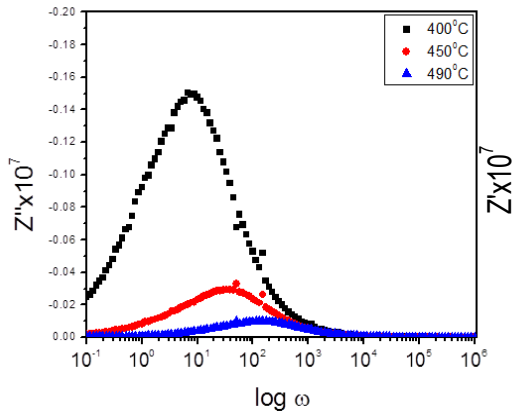


Fig-7

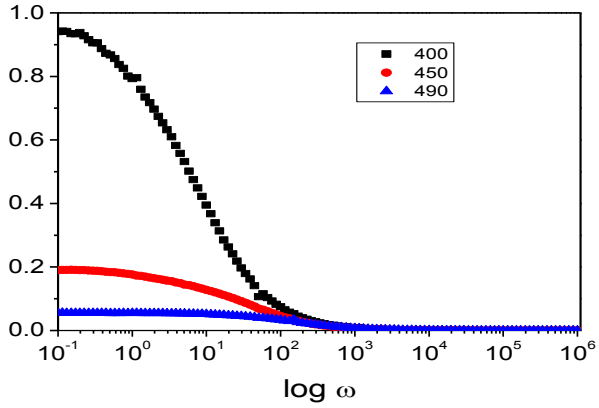


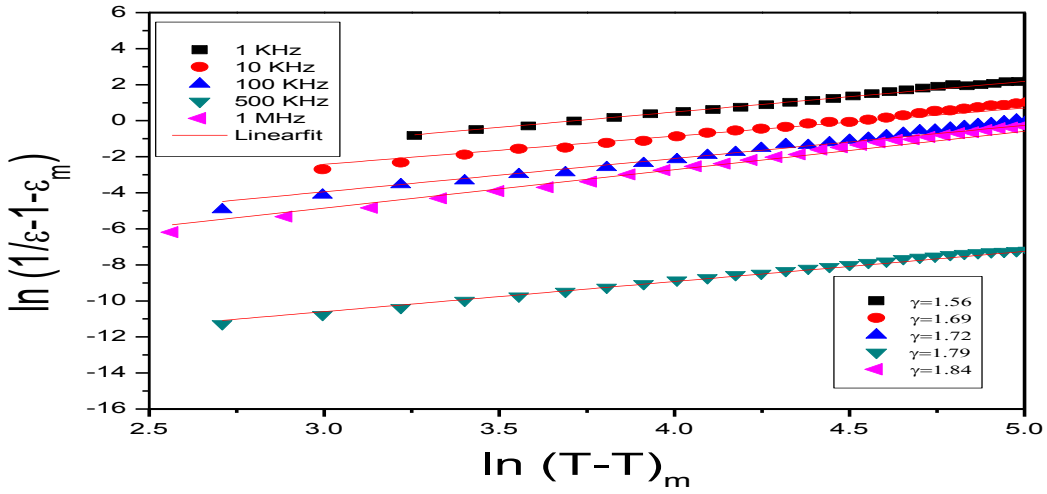
fig-8

4.2.4 MODIFIED CURIE-WEISS LAW:

The modified Curie- Weiss law is given by $1/\varepsilon - 1/\varepsilon_m = (T - T_m)^{\gamma}/C$

slope gives γ value which is the diffusivity of the material. If γ value lies between 1.5 to 2 , then the relaxor behaviour of ferroelectric material will be satisfied.From the table below, it is confirmed that BBT is relaxor in nature.

Fig-9



frequency	Ɛ’	**Ɛ’ (RT)**	**T_m**	**γ**
1kHz	3221	361	444	1.56
10KHz	2762	341	450	1.69
100KHz	2619	333	455	1.72
500KHz	2508	330	458	1.79
1MHz	2380	323	462	1.84

4.2.5 P-E LOOP:

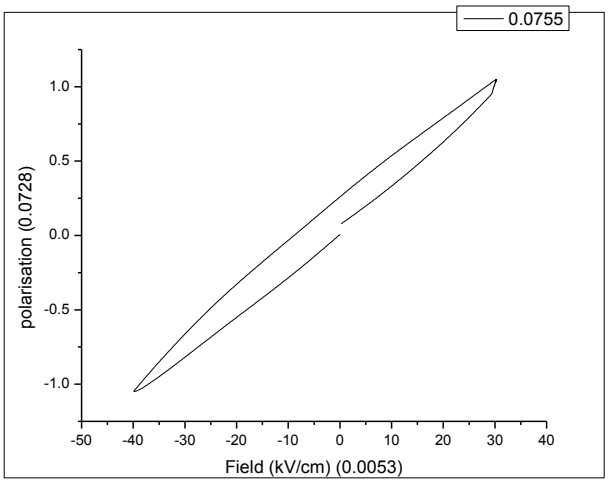


Fig-10

P-E loop of the samples were measured using a conventional Sawyer-Tower circuit. The area of the loop is very thinner of the hysteresis loop confirmed the relaxor property of ferroelectric nature of BBT.

The P_r value is found to be $0.0083\mu C/m^2$

CHAPTER-5

CONCLUSION:

Barium bismuth Titanate($BaBi_4Ti_4O_{15}$) was prepared with single phase when calcined at 1000^oC .When sintered with 1hr and 2 hr at 1100^oC no impurity phase appears .Well grain growth appeared for 2hrs sintering duration .Dielectric measurement showed the relaxor behaviour of the material .The value of diffusivity γ obtained from modified curie-weiss law ranging from 1.56 to 1.84 confirmed the same. The slim P-E loop appear also is confirmation of relaxor nature.All these results of various characterization confirms BBT as a relaxor ferroelectric material.

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G.C.C da coasta,A.z.simoes,A.Ries,C.R.Foschini,M.A Zaghete,J.A.Varela
(Bi2O2)2+(Ax-1BxO3x+1)2-

X=No.of pervoskite building block between two (bi2O2)2+ layers and A & B represents the different cations with low and high value in structure.

13) Phase transition in ABi4Ti4O15 (A=Ca,Sr,Ba) Aurivillius oxides prepared through a soft chemical route.

S.K Rout, E.sinha, A.Hussain, J.S Lee, C.W. Ahn, I.W**.**Kim and S.I.woov.